Ultrasonic relaxation studies in aqueous surfactants
3.1. INTRODUCTION:

Ultrasonic techniques are being employed to gain some insight into the molecular behavior of solutions and liquid mixtures. These are considered to be nondestructive tools when low amplitude waves are used. The study of propagation of ultrasonic waves in aqueous biological solutions is to understand the nature of interaction between biologically active substances and water, since the latter plays a key role in living organisms. The ultrasonic velocity and absorption are sensitive to any structural changes, such as micelle formation, stacking and transformation from spherical to rod-like shapes of micelle that occur in the surfactant solutions. The ultrasonic studies on aqueous solutions of biological surfactants such as bile salts are scanty and also to get more insight into the above aspects, the present work is undertaken in aqueous surfactants (biologically important bile acids) viz., taurocholic acid and taurodeoxycholic acid.

3.1.2. SURFACTANT:

Surfactant or surface-active agents are amphiphilic. The name amphiphile is sometimes used synonymously with surfactant. The word is derived from Greek word amphi, meaning both, and the term relates to the fact that all surfactant molecules consist of at least two parts, one, which is soluble in a specific fluid (the lyophilic part) and one, which is insoluble (the lyophobic). Because of these characteristics, they are widely used in industrial application to stabilize dispersions such as foams, emulsions and suspensions. The association of many classes of surface-active molecules into micellar aggregation is a well-known phenomenon.

Surfactant molecules (also called amphiphiles or detergents) unite a polar or ionic head and a nonpolar tail within the same molecule (figure 3.1a). The nonpolar part, which is typically made up of one or more alkyl chains, causes these compounds
Figure 3.1a A surfactant molecule

- **Head group**
- **Non-polar (Hydrophobic)**
- **Hydrocarbon tail**
- **Polar (Hydrophilic)**
to be sparingly soluble in water, whereas the polar or ionic part interacts strongly with water.

3.1.3. TYPES OF SURFACTANTS:

There are four main classes of surfactants namely anionic, cationic, non-ionic and zwitterionic. Surfactants are grouped into one of these categories depending on the nature of the head group.

- **Anionic surfactants**
- **Cationic surfactants**
- **Zwitterionic surfactants**
- **Non-ionic surfactants**

In anionic surfactants, the surface active species is the anion, as in Sodium Dodecyl Sulfate, \( CH_3(CH_2)_10SO_4^-Na^+ \).

In cationic surfactants, the surface active species is positively charged, as in dodecylamine hydrochloride, \( CH_3(CH_2)_11^+NH_3Cl^- \).

Zwitterionic surfactants have two ionogenic groups producing a cation and an anion. Zwitterionic surfactants can be ampholytic and can behave as either cationic, anionic, or non-ionic species depending on the pH of the solution, an example is N-dodecyl-N,N-dimethyl betaine, \( C_{12}H_{25}N^+(CH_3)_2CH_2COO^- \).

Non-ionic surfactants have uncharged head groups which are however polar in nature. These head groups are usually based on a polyoxyethylene chain. An example is polyethyleneglycol mono [4-(1, 1, 3, 3-tetramethylbutyl) phenyl] ether. This surfactant is also available commercially under the name TritonX-100. In these
surfactants, the head group is usually larger than the hydrocarbon tail. Non-ionic surfactants, though, with small head groups also exist, such as dodecyl sulfinyl ethanol ($C_{12}H_{25}SOCH_{2}CH_{2}OH$).

### 3.1.4. STRUCTURE OF A MICELLE:

In the past couple of decades, the recognition that surfactant association structures can mimic biological structures has sparked considerable interest in self-assembled surfactant aggregates such as cylindrical, lamellar, and reverse micelles [1]. Enzymes, for example, are protein molecules into which a substrate fits to form a reactive intermediate. The highly efficient and specific catalytic effect of enzymes makes their investigation an interesting area of biomedical and detergent research (as enzymes are often added to laundry detergents to improve performance) [2, 3]. Likewise, cell membranes not only compartmentalize biological systems but also perform a variety of functions in cellular biochemical and physiological processes. Surfactant structures can be used as model systems to mimic both enzymes and membranes. Lipid aggregates known as liposomes are common in physiological systems, and specially designed liposomes are used, for example, as drug-delivery vehicles or in cosmetics [4]. Self-assembled structures such as micelles or reversed micelles (surfactant aggregates with hydrophilic head groups shielded from and lipophilic tails sticking out to an organic solvent) also play an increasingly important role in catalysis and separation processes in engineering and environmental science and technology [5–7].

A theory of micellar structure, based upon the geometry of various micellar shapes and the space occupied by the hydrophilic and hydrophobic groups of the surfactant molecules, has been developed by Israelachvili et al. and Mitchell and Ninham [8, 9]. In aqueous media, for example, surfactants with bulky or loosely packed hydrophilic groups and long, thin hydrophobic groups tend to form spherical micelles,
while those with short, bulky hydrophobic groups and small, close-packed hydrophilic groups tend to form lamellar or cylindrical micelles. At concentrations slightly above the critical micelle concentration (CMC), micelles are considered to be of spherical shape [10]. Changes in temperature, surfactant concentration, or additives in the solution may change the size, shape, aggregation number, and stability of the micelles. The structure of a micelle could vary from spherical to rod- or disc-like to lamellar. In concentrated solutions (much higher than the CMC) lamellar micelles form, such that water molecules occupy the region between parallel sheets of surfactants. Micelles may also form long cylinders packed together (known as lyotropic mesomorphs or liquid crystalline phases) at high surfactant concentrations [11, 12]. The structure and stability of micelles significantly influence the dynamic properties of the system.

3.1.5. MICELLIZATION:

Since the beginning of the study of surfactant solutions, it has been recognized that the physical properties of surfactant solutions, such as ultrasonic velocity, surface tension, osmotic pressure, electrical conductivity, and solubility (as a function of temperature), show an abrupt change in the neighborhood of a critical concentration, when surfactant aggregation begins to occur. This unusual behavior of fatty acid salts in dilute aqueous solution is first investigated by McBain [13, 14] and later by Hartley [15]. Other evidence for molecular aggregation has been obtained from vapor pressure measurements and the solubility of organic material. The formation of colloidal-sized clusters of individual surfactant molecules in solution is now better known as micellization.

Although first suggested by McBain [13], the earliest concrete model for spherical micelles is attributed to Hartley et al. [16]. A schematic representation of a spherical micelle is given in figure 3.1b. In a typical surfactant solution, surfactant molecules disperse as monomers in the aqueous phase, form aggregates (micelles), or adsorb as a
Figure 3.1b Schematic representation of a micelle
film at the air/liquid interface and at the solid/liquid interface of the container. The surfactant is in dynamic equilibrium between these states, implying that the rates of adsorption and desorption are equal. Thus, at a given temperature, pressure, and concentration, the number of monomers adsorbed at the air/water interface and the number of monomers and micelles present in solution is fixed under equilibrium conditions. The concentration of monomers and micelles changes with equilibrium conditions such as pressure, temperature, or surfactant and salt concentration.

The process of surfactant clustering or micellization is primarily an entropy-driven process [17, 18]. When surfactants are dissolved in water, the hydrophobic group disrupts the hydrogen-bonded structure of water and therefore increases the free energy of the system. Surfactant molecules therefore concentrate at interfaces, so that their hydrophobic groups are removed or directed away from the water and the free energy of the solution is minimized. The distortion of the water structure can also be decreased (and the free energy of the solution reduced) by the aggregation of surface-active molecules into clusters (micelles) with their hydrophobic groups directed toward the interior of the cluster and their hydrophilic groups directed toward the water. However, the surfactant molecules transferred from the bulk solution to the micelle may experience some loss of freedom from being confined to the micelle. In addition, they may experience an electrostatic repulsion from other similarly charged surfactant molecules in the case of surfactants with ionic head groups. These forces increase the free energy of the system and oppose micellization. Hence, micelle formation depends on the force balance between the factors favoring micellization (van der Waals and hydrophobic forces) and those opposing it (kinetic energy of the molecules and electrostatic repulsion). The explanation for the entropy-dominated association of surfactant molecules is called the “hydrophobic effect” or “hydrophobic bonding” [19].

The concentration at which micelles first appear in solution is called the critical micelle concentration (CMC) and can be determined from the discontinuity or inflection
point in the plot of a physical property of the solution as a function of the surfactant concentration [20, 21]. Beyond this concentration, the addition of more surfactant molecules will result in an increase in the number of micelles, while the concentration of monomeric surfactant remains almost constant. Micellization is usually driven by an increase in entropy, resulting from the liberation of the water molecules from the hydrophobic hydration shells of the monomeric amphiphile molecules, whereas the enthalpy change is generally close to zero [22].

Representing the surfactant by $S$, the micellization process can be described by the reaction

$$nS \leftrightarrow S_n$$

where $S_n$ is a micellar aggregate composed of $n$ surfactant molecules. The so-called aggregation number $n$ (which represents the number of surfactant molecules in a micelle) has been found to increase with increasing length of the hydrophobic group and decrease with increasing size of the hydrophilic group [23]. In general, the greater the hydrocarbon chain length of the surfactant molecules, the greater the aggregation number of micelles. Also, those factors that increase the aggregation number tend to decrease the CMC. For example, increasing the alkyl chain length of a surfactant decreases the CMC. The presence of electrolyte also decreases the CMC, due to the so-called "salting out" effect. The work required to accommodate a nonpolar solute in a given volume of water is increased in electrolyte solution because of strong water/ion interactions. When surfactant monomers are salted out by the presence of an electrolyte, micellization is favored and the CMC is decreased. Another factor favoring micellization in electrolyte solutions is the shielding of charges between ionic head groups (in the case of ionic surfactants) [23]. It is important to emphasize that CMC represents the concentration of free surfactant monomers in a micellar solution under given conditions of temperature, pressure and composition.
3.1.6. DYNAMIC PROPERTIES OF SURFACTANT SOLUTIONS:

Micelles are extremely dynamic aggregates. Ultrasonic, temperature and pressure jump techniques have been employed to study the rate constants associated with the different equilibria involved. Rates of uptake of monomers into micellar aggregates are close to diffusion controlled [24]. The residence times of the individual surfactant molecules in the aggregate are typically in the order of $10^{-5} - 10^{-6}$ seconds [24, 25], whereas the lifetime of the micellar entity is about $10^{-3} - 10^{-1}$ seconds [24b, 25b]. Factors that lower the CMC usually increase the lifetimes of the micelles as well as the residence times of the surfactant molecules in the micelle [26]. Due to this dynamic character, the size and shape of micelles are subjected to appreciable structural fluctuations. Hence, micellar aggregates are polydisperse, as is demonstrated by small-angle neutron scattering data [27]. Average aggregation numbers are typically in the range of 40 – 100 [28]. The highly dynamic character has for a long time successfully misled chemists in their conception of the structure of a micelle.

The association of many classes of surface-active molecules into micellar aggregates is a well-known phenomenon. Micelles are often drawn as static structures of spherical aggregates of oriented surfactant molecules. However, micelles are in dynamic equilibrium with individual surfactant molecules that are constantly being exchanged between the bulk and the micelles. Additionally, the micelles themselves are continuously disintegrating and reassembling.

There are two relaxation processes involved in micellar solutions [29–53]. The first is a fast relaxation process referred to as $\tau_1$ (generally of the order of microseconds), which is associated with the quick exchange of monomers between micelles and the surrounding bulk phase. This process can be considered to be the collision between surfactant monomers and micelles. The second relaxation time, $\tau_2$ (of the order of milliseconds), is attributed to the micelle formation and dissolution process (i.e., the
lifetime of the micelle). It has been shown that in certain surfactants such as nonionic surfactants and mixed surfactant systems, \( \tau_2 \) can be as long as minutes. For example, the \( \tau_2 \) of a 0.80 mM solution of the nonionic surfactant Synperonic A7 is 150s [30]. Figure 3.1c shows the two characteristic relaxation times, \( \tau_1 \) and \( \tau_2 \), associated with micellar solutions. Micelle formation and disintegration is analogous to the equilibrium between water and water vapor at a given temperature and pressure. For a closed system containing liquid water and water vapor in equilibrium, the number of water molecules per unit area per second evaporating from the surface is equal to the number of water molecules condensing at the surface. Thus, the total number of molecules in the vapor phase or in the liquid does not change with time, so the rate of condensation is equal to the rate of evaporation. The same principle holds for a micellar solution. Under equilibrium conditions, the rate of micelle formation is equal to the rate of disintegration into surfactant monomers.

Micellar relaxation kinetics shows dependence on temperature, pressure, and concentration, as well as on the addition of other species such as short-chain alcohols. It has been shown that the \( \tau_2 \) of an SDS micelle decreases with increased concentration of C1–C6 alcohols [54]. This kinetics has been studied by various techniques such as stopped-flow, temperature-jump, pressure jump, and ultrasonic absorption [29-36]. The two relaxation times can be used to calculate two important parameters of a micellar solution: (a) the residence time of a surfactant molecule in a micelle and (b) the average lifetime or stability of a micelle.

3.1.7. BILE SALTS:

Bile salts are natural surfactants mainly stored in the gall bladder. Their function is essentially the emulsification and transport of food fats and lipids. The physicochemical properties of bile salts are of interest because of their very important
Fast Relaxation time, microseconds

\[ \text{Fast Relaxation time, microseconds} \]

Slow relaxation time, milliseconds

\[ \text{Slow relaxation time, milliseconds} \]

Figure 3.1c Mechanisms for the two relaxation times, \( \tau_1 \) and \( \tau_2 \), for a surfactant solution above CMC
role in the metabolic process of absorption at the intestinal level. Bile salts are different from common surfactants, which in general have their polar head group attached to a flexible hydrocarbon chain, but bile salts have a rigid steroid backbone, having up to three hydroxyl groups and a branched linear chain ended by a carboxylate group, which may or may not be conjugated with glycine or taurine. This difference in structure generates a typical aggregation behavior.

The bile salts are naturally occurring detergents which form micellar aggregates in aqueous solution [55]. Bile salts are synthesized in the liver. They form aggregates (micelles) which help to solubilize and disperse dietary lipids in the small intestine. Bile salts have also been studied in recent years as alternative to conventional detergents for chemical analysis. Specific areas of application include chemical separations [56] and luminescence analysis [57]. The bile salt micelles are smaller and more rigid than those of conventional detergents resulting in unique aggregation behavior with respect to self association as well as solubilization of hydrophobic molecules in aqueous solution [58–60]. Bile salts are nearly flat molecule with a hydrophobic and a hydrophilic surface. Oakenfull et al [61] have carried out equivalent conductance and apparent molar volume studies on aqueous and aqueous–ethanolic solutions of sodium cholate, sodium deoxycholate and sodium lithocholate. Their studies established that the first stage in the formation of bile salt micelles is the formation of hydrogen bonded dimers and the hydrogen bonding is the major interaction associated with the formation of dimers. Information about the formation and structure of these micelles is needed to develop a further understanding of the physiological role of the bile salts. From a survey of literature available, it can be seen that most of the ultrasonic studies are only on aqueous and aqueous–alcoholic solutions of some ionic and non-ionic surfactants [61–69].

The ultrasonic relaxation studies of Aicart et al [68] on mixed micelles of the cationic surfactant Decyltrimethyl ammoniumbromide (DTAB) and alcohol show that
the micelle kinetics of DTAB is affected by the presence of propanol. Their results indicate that the exit rate of DTAB monomer from micelles decreases with the addition of propanol. This behavior is believed to be due to the decrease in the charge density at the surface of the mixed micelle and results from the presence of propanol around the surface of the micelle. A similar relaxation studies of Kato et al. [62] in octyl- decyl- and tetra- decyltrimethyl ammoniumbromide in aqueous solution over the frequency range 0.2 – 210 MHz reveals that the ultrasonic relaxation spectra show single relaxation process for all the solutions and at all the concentrations investigated. The observed relaxation process is described to fast relaxation due to the exchange process of a surfactant monomer between micelle and the surrounding bulk solution.

The ultrasonic studies on aqueous solutions of biological surfactants such as bile salts are scanty and hence it may be worthwhile to study the molecular interactions in these solutions using a non-destructive technique like ultrasonic method. The acoustical relaxation studies in aqueous solutions of sodium taurocholate by G. Ravichandran et al. [84] successfully extended the general kinetic model of micelle formation developed by Aniansson and Wall [24b, 80] and Teubner [87] for ordinary detergents to a biological detergent namely sodium taurocholate. In order to extend the same to other bile acids, the present work is undertaken in aqueous surfactants (biologically important bile acids) viz., taurocholic acid and taurodeoxycholic acid in the concentration range of 0.001 - 0.010 mol dm$^{-3}$ and over the frequency range of 3 – 89 MHz.
3.2. RESULTS AND DISCUSSION:

3.2.1. TAUROCHOLIC ACID:

Chemical name: 2-[(3alpha, 5beta, 7alpha, 12alpha) - 3, 7, 12 - trihydroxy - 24 - oxocholan-24-yl] amino] ethanesulfonic acid (C_{26}H_{45}NO_{7}S).

The product of conjugation of cholic acid with taurine is taurocholic acid. Its sodium salt is the chief ingredient of the bile of carnivorous animals. Sodium salt is a lipase accelerator.

A crystalline acid, taurocholic acid involved in the emulsification of fats and occurring as a sodium salt in the bile of humans, oxen and other mammals.

The product of conjugation of cholic acid with taurine. Its sodium salt is the chief ingredient of the bile of carnivorous animals. It acts as a detergent to solubilise fats for absorption and is itself absorbed. It is used as a cholagogue and choleretic.

3.2.2. TAURODEOXYCHOLIC ACID:


A bile salt formed in the liver by conjugation of deoxycholate with taurine, usually as the sodium salt. It is used as a cholagogue and choleretic, also industrially as a fat emulsifier.

3.2.3. ULTRASONIC VELOCITY STUDIES:

The bile acids, taurocholic acid and taurodeoxycholic acid are procured from M/S Aldrich-sigma chemicals and are used as such without further purification. Aqueous solutions of taurocholic and taurodeoxycholic acid are prepared in the concentration range of 0.001-0.010 mol dm^{-3} by dissolving known amount of the solute in
fixed volume of double distilled water. The ultrasonic velocity is measured using an Ultrasonic Time Intervalometer (UTI-101) by Pulse Echo Overlap Method (PEO) in the frequency of 10 MHz as given in Chapter II. The density and viscosity of the solutions are measured using Specific Gravity Bottle and Ostwald’s Viscometer as given in Chapter II. The temperature of the solutions is maintained at 303 K by circulating water from a thermostatically controlled water bath with an accuracy of ±0.1 K. The temperatures of the solution and the circulated water are noted by using a dual terminal digital thermometer by inserting them in the provided holes in the ultrasonic liquid cell for this purpose.

From the measured values of velocity, density and viscosity, the parameters viz., adiabatic compressibility, classical absorption and free length of the solutions are computed using the standard relations given in Chapter I.

The ultrasonic velocity, adiabatic compressibility, density, shear viscosity, classical absorption and free length in the concentration range of 0.001-0.010 mol dm$^{-3}$ solution is given in tables 3.1 and 3.2 for taurocholic acid and taurodeoxycholic acid respectively. The variation of ultrasonic velocity with concentration is shown in figures 3.1 and 3.2 for taurocholic acid and taurodeoxycholic acids respectively. The variation of adiabatic compressibility with concentration is shown in figures 3.3 and 3.4 for taurocholic acid and taurodeoxycholic acids respectively.

From figure 3.1, it can be seen that the ultrasonic velocity in aqueous solutions of taurocholic acid increases with increasing concentration. The variation of ultrasonic velocity with concentration has shown an inflection at 0.007 molar concentration of taurocholic acid.

From figure 3.2, it can be seen that the ultrasonic velocity in aqueous solutions of taurodeoxycholic acid increases with increasing concentration taurodeoxycholic acid up to 0.004 mol dm$^{-3}$ and decreases at 0.005 mol dm$^{-3}$ and again increases as the concentration
Figure 3.1 Variation of ultrasonic velocity with concentration for aqueous taurocholic acid
Figure 3.2 Variation of ultrasonic velocity with concentration for aqueous taurodeoxycholic acid
Figure 3.3 Variation of adiabatic compressibility with concentration for aqueous taurocholic acid
Figure 3.4 Variation of adiabatic compressibility with concentration for aqueous taurodeoxycholic acid.
taurodeoxycholic acid increases further. It has shown a discontinuity at 0.004 mol dm$^{-3}$ concentration of taurodeoxycholic acid.

From figure 3.3, it can be seen that the adiabatic compressibility in aqueous solutions of taurocholic acid decreases with increasing concentration of taurocholic acid in the concentration range 0.001 – 0.010 mol dm$^{-3}$. The variation of adiabatic compressibility with concentration has shown an inflection at 0.007 mol dm$^{-3}$ concentration of taurocholic acid.

From figure 3.4, it can be seen that the adiabatic compressibility in aqueous solutions of taurodeoxycholic acid decreases with increasing concentration taurodeoxycholic acid upto 0.004 molar and decreases at 0.005 mol dm$^{-3}$ and again increases as the concentration taurodeoxycholic acid increases further in the concentration range 0.001 – 0.010 mol dm$^{-3}$. It has shown a discontinuity at 0.004 mol dm$^{-3}$ concentration of taurodeoxycholic acid.

The variation of intermolecular free length follows the above pattern with concentration for taurocholic acid and taurodeoxycholic acid in the concentration range 0.001 – 0.010 molar.

The salient features of the ultrasonic velocity studies are,

- **Aqueous Taurocholic Acid:**
  - The ultrasonic velocity increases with increasing concentration of taurocholic acid and shows an inflection at 0.007 mol dm$^{-3}$ concentration of taurocholic acid
  - The adiabatic compressibility decreases with increasing concentration of taurocholic acid and shows an inflection at 0.007 mol dm$^{-3}$ concentration of taurocholic acid as seen in the ultrasonic velocity profile
  - The free length decreases with increasing concentration of taurocholic acid
  - The density of the solution is increased with increasing concentration of taurocholic acid
✓ The shear viscosity increases with increasing concentration of taurocholic acid, but it initially decreases below the value of solvent distilled water.

✓ The classical absorption is showing a non-linear variation in the concentration range studied.

➢ Aqueous Taurodeoxycholic Acid:

✓ The ultrasonic velocity increases with increasing concentration of taurodeoxycholic acid up to 0.004 mol dm$^{-3}$, it decreases at 0.005 mol dm$^{-3}$ concentration, and again increases as the concentration increases, and shows a discontinuity at 0.004 mol dm$^{-3}$ concentration of taurodeoxycholic acid.

✓ The adiabatic compressibility decreases with increasing concentration of taurodeoxycholic acid up to 0.004 mol dm$^{-3}$, it increases at 0.005 mol dm$^{-3}$ concentration, again decreases as the concentration increases, and shows a discontinuity at 0.004 mol dm$^{-3}$ concentration of taurodeoxycholic acid.

✓ The free length decreases with increasing concentration of taurodeoxycholic acid up to 0.004 mol dm$^{-3}$, it increases at 0.005 mol dm$^{-3}$ concentration and again decreases as the concentration increases.

✓ The density of the solution is increased with increasing concentration of taurodeoxycholic acid.

✓ The shear viscosity increases with increasing concentration of taurodeoxycholic acid, but it initially decreases below the value of solvent distilled water.

✓ The classical absorption is showing a non-linear variation in the concentration range studied.

The ultrasonic velocity is higher in aqueous taurocholic acid and taurodeoxycholic acid solution compared to water and indicates interaction between...
solute and solvent molecules [70]. From figure 3.1, the ultrasonic velocity increases with increasing concentration of taurocholic acid. When taurocholic acid is dissolved in water, it dissociates into sodium ion and taurocholic acid monomers. The water structure is broken and more monomers are released for association with taurocholic acid molecules. This strengthens the medium and ultrasonic velocity shows an increase from that of water and it continues to increase as the concentration is changed and the ultrasonic velocity shows a non linear increase and indicating an inflection at the 0.007 mol dm$^{-3}$ concentration. The non-linear increase in the ultrasonic velocity is due to the formation of hydrogen bonds between the free hydroxyl groups of taurocholic acid and the water molecules. According to Oakenfull et al [61], the first stage in the formation of bile salt micelles is the formation of hydrogen bonded dimers. Further aggregation of micelle can take place by polyfunctional hydrogen bonding.

The $Na^+$ ion obtained due to the dissociation of taurocholic acid in aqueous medium may also contribute towards the increase of ultrasonic velocity by its water structure making property. The occurrence of the inflection point at 0.007 mol dm$^{-3}$ concentration of taurocholic acid corresponds to the critical micelle concentration (CMC) of aqueous taurocholic acid. A similar behavior is observed from the variation of concentration with adiabatic compressibility for aqueous taurocholic acid (figure 3.3). The increase of ultrasonic velocity when the concentration of taurocholic acid increases beyond the critical micelle concentration may be due to aggregation of taurocholic acid molecules leading to micelle formation. Above critical micelle concentration, aggregation of molecules can take place by polyfunctional hydrogen bonding. Since, the taurocholic acid molecule has both residual hydrogen bond donors, acceptor groups, polyfunctional hydrogen bonding may be possible, and this may perhaps leads to the formation of aggregates. This formation of aggregates led to an increase of ultrasonic velocity and decrease of adiabatic compressibility as reported by Varma [63] and Mehrotra [64]. Such an increase and decrease in ultrasonic velocity and adiabatic
compressibility is observed in the present study, when the concentration of taurocholic acid in water is increased above the CMC value. The decrease in intermolecular free length with concentration generally indicates strong interaction between solute and solvent molecules [71].

The ultrasonic velocity increases up to 0.004 mol dm$^{-3}$ concentration and decreases at 0.005 mol dm$^{-3}$ concentration of taurodeoxycholic acid and again increases as the concentration of taurodeoxycholic acid increases. The occurrence of the discontinuity at 0.004 mol dm$^{-3}$ concentration of taurodeoxycholic acid corresponds to the critical micelle concentration (CMC) of aqueous taurodeoxycholic acid. A similar behavior obtained from the variation of concentration with adiabatic compressibility for aqueous taurodeoxycholic acid (figure 3.1). The decrease in the ultrasonic velocity at 0.005 mol dm$^{-3}$ concentration or above the critical micelle concentration may attributed to the behavior of $Na^+$ ion. The $Na^+$ ion restricts the overall motional freedom of dense monomers, and thereby the water clusters try to aggregate around the hydrophobic taurodeoxycholic ion due to hydrophobic interaction. So, the medium becomes more compressible and hence the velocity decreases and the adiabatic compressibility increases. This indicates that the hydrophobic interaction might be dominating over the structure making property of $Na^+$ ions in aqueous solutions of taurodeoxycholic acid at concentration of 0.005 mol dm$^{-3}$. The increase in ultrasonic velocity after 0.005 mol dm$^{-3}$ may be due to micelle formation taking place in these solutions as the concentration of taurodeoxycholic acid is increased.

It is well known that addition of small amounts of hydrogen bonded solutes to water increases the sound velocity of solutions well above the values in pure components. This behavior is well evidenced, for example, the presence of maxima in the sound velocity versus concentration plots (at fixed temperatures) observed in monohydric alcohols [72, 73] and alkoxyethanols [74, 75]. On the other hand, in
aqueous solutions of ionic surfactants, the sound velocity increases almost linearly with the surfactant concentration up to the CMC and thereafter it again increases or decreases about linearly [76, 77] with a discontinuity at CMC. Depending on the surfactant species, the slopes can be different and the break point at CMC more or less sharp.

Further when the micelles are known to form, there is a competition between micelles proper and pre as well as post micellar formation. The formation is different for different surfactant molecules and hence the observed CMC is different for the two surfactant systems in the present study. Since there is a competition between micelles proper and dense monomer population, absorption studies may yield some insight into the mechanism.

3.2.4. ULTRASONIC ABSORPTION STUDIES:

The ultrasonic absorption studies are carried out in the aqueous solutions of taurocholic acid and taurodeoxycholic acid in the frequency range of 3-89 MHz using Pulsed Power Oscillator and MATEC 7700 system as given in Chapter II. Aqueous solutions of taurocholic and taurodeoxycholic acid are prepared in the concentration range of 0.001-0.010 by dissolving known amount of solute in fixed volume of double distilled water. The temperature of the solutions is maintained at 303K by circulating water from a thermostatically controlled water bath with an accuracy of ±0.1K. The temperatures of the solution and the circulated water are noted by using a dual terminal digital thermometer by inserting them in the provided holes in the ultrasonic liquid cell for this purpose.

From the value of absorption coefficient (\(\alpha\)), the observed absorption \(\left(\frac{\alpha}{f^2}\right)_{obs}\) is computed. These absorption data are fitted to the conventional Debye type single relaxation equation in the frequency range studied using the non-linear least square
fitting algorithm proposed D. W. Marquardt [78]. The non-linear fitting program is written in FORTRAN language [79] and is given in appendix A. From the computation of non-linear fitting program, the relaxation amplitudes A & B, the relaxation frequency \( f \), and absorption per wavelength \( (\alpha \lambda) \) are computed. From the values of the computed parameters, the relaxation time \( \tau \) is calculated using the relation,

\[
\tau = \left( \frac{1}{2 \pi f} \right)
\]

The maximum absorption per wavelength \( (\alpha \lambda)_{\text{max}} \) is calculated using the relation,

\[
(\alpha \lambda)_{\text{max}} = \left( \frac{Af \mu}{2} \right)
\]

The computed parameters viz, relaxation frequency \( f \), relaxation amplitudes A & B, relaxation time \( \tau \) and maximum absorption per wavelength \( (\alpha \lambda)_{\text{max}} \) for aqueous taurocholic acid and taurodeoxycholic acid in the concentration range 0.001 to 0.010 mol dm\(^{-3}\) are given in tables 3.3 and 3.4.

The variation of observed absorption \( \left( \frac{\alpha}{f^2} \right)_{\text{obs}} \) for individual concentration and the absorption per wavelength \( (\alpha \lambda) \) with frequency for all concentrations are given graphically in figures 3.5 – 3.16.

Figures 3.5 – 3.14 shows the variation of observed absorption with frequency for aqueous solutions of taurocholic acid and taurodeoxycholic acid in the concentration range 0.001 to 0.010 mol dm\(^{-3}\). The nature of the variation is different from that of ultrasonic velocity. The observed absorption decreases with increasing frequency. The experimentally measured values of absorption \( \left( \frac{\alpha}{f^2} \right)_{\text{obs}} \) are plotted as open circles in the figures 3.5 – 3.14. These experimental points fits very well to the equation for single relaxation as indicated by the continuous line in figures 3.5 – 3.14 and thereby giving the information that aqueous bile acids studied shows a single relaxation behavior in
Figure 3.5 Variation of observed absorption with frequency for 0.001 \text{ mol dm}^{-3} and 0.002 \text{ mol dm}^{-3} aqueous taurocholic acid
Figure 3.6 Variation of observed absorption with frequency for 0.003 and 0.004 aqueous taurocholic acid.
Figure 3.7 Variation of observed absorption with frequency for 0.005 and 0.006 molar aqueous taurocholic acid.
Figure 3.8 Variation of observed absorption with frequency for 0.007 and 0.008 mol dm$^{-3}$ aqueous taurocholic acid
Figure 3.9 Variation of observed absorption with frequency for 0.009 and 0.010 moles/L aqueous taurocholic acid
Figure 3.10 Variation of observed absorption with frequency for 0.001 and 0.002 mol dm$^{-3}$ aqueous taurodeoxycholic acid.
Figure 3.11 Variation of observed absorption with frequency for 0.003 and 0.004 aqueous taurodeoxycholic acid
Figure 3.12 Variation of observed absorption with frequency for $0.005 \text{ and } 0.006 \text{ mol/L aqueous taurodeoxycholic acid}$
Figure 3.13 Variation of observed absorption with frequency for 0.007 and 0.008 mol aqueous taurodeoxycholic acid.
Figure 3.14 Variation of observed absorption with frequency for 0.009 and 0.010 mol\textsuperscript{1} L\textsuperscript{-1} aqueous taurodeoxycholic acid.
the concentration range studied and in the frequency range 3 - 89 MHz. The variation of observed absorption shows a non-linear behavior with increasing concentration of taurocholic acid and taurodeoxycholic acid. It can also be seen that the values of observed absorption increases in magnitude with increase in concentration of taurocholic acid and taurodeoxycholic acid and it is high in taurodeoxycholic acid than taurocholic acid.

The variation of absorption per wavelength (αl) with increasing frequency (calculated) is given graphically in figures 3.15 and 3.16 for taurocholic acid and taurodeoxycholic acid respectively. From the figures, it can be seen that the absorption per wavelength for the aqueous solutions of taurocholic acid and taurodeoxycholic acid increasing with increasing frequency and reaches a maximum value at a particular frequency called relaxation frequency \( f_r \) of that particular concentration and then decreases further increase in frequency. For any particular frequency, the absorption per wavelength has shown a non-linear variation with increase in concentration taurocholic acid and taurodeoxycholic acid. Also, the relaxation frequency \( f_r \) increases to a higher value with increase in the concentration of taurocholic acid and taurodeoxycholic acid.

The salient features of the ultrasonic absorption studies are,

- **Aqueous Taurocholic Acid:**
  - The value of observed absorption shows a non-linear variation with increase in concentration of taurocholic acid in water
  - The observed absorption \( \left( \frac{\alpha}{f^2} \right)_{obs} \) decreases with increase in frequency for any particular concentration of taurocholic acid
Figure 3.15 Variation of absorption per wavelength with frequency for aqueous taurocholic acid
Figure 3.16 Variation of absorption per wavelength with frequency for aqueous taurodeoxycholic acid
For any particular concentration of taurocholic acid, the variation of absorption per wavelength \((\alpha \lambda)\) shows a maximum at the relaxation frequency \(f_r\) of that particular concentration.

The values of absorption per wavelength \((\alpha \lambda)\) show a non-linear variation with increasing concentration of taurocholic acid.

The relaxation frequency \(f_r\) shifts towards a higher value with increase in concentration of taurocholic acid and it lies the frequency range of 8.75 MHz – 13.13 MHz.

The relaxation time \(\tau\) shifts towards a lower value with increase in concentration of taurocholic acid.

The relaxation amplitudes \(A\) & \(B\) shown a non-linear variation in the concentration range studied for taurocholic acid and relaxation amplitude \(A\) shifts towards a lower value with increase in concentration of taurocholic acid.

**Aqueous Taurodeoxycholic Acid:**

The value of observed absorption shows a non-linear variation with increase in concentration of taurodeoxycholic acid in water.

The observed absorption \(\left(\frac{\alpha}{f^2}\right)_{obs}\) decreases with increase in frequency for any particular concentration of taurodeoxycholic acid.

For any particular concentration of taurodeoxycholic acid, the variation of absorption per wavelength \((\alpha \lambda)\) shows a maximum at the relaxation frequency \(f_r\) of that particular concentration.

The values of absorption per wavelength \((\alpha \lambda)\) show a non-linear variation with increasing concentration of taurodeoxycholic acid.
The relaxation frequency $f$, shifts towards a higher value with increase in concentration of taurodeoxycholic acid and it lies the frequency range of $8.45 \text{ MHz} - 13.06 \text{ MHz}$.

The relaxation time $\tau$ shifts towards a lower value with increase in concentration of taurodeoxycholic acid.

The relaxation amplitudes $A$ & $B$ shown a non-linear variation in the concentration range studied for taurodeoxycholic acid and relaxation amplitude $A$ shifts towards a lower value with increase in concentration of taurodeoxycholic acid.

The aqueous surfactant solutions forms micelles at CMC and there is a dynamic exchange process occurring between surfactant monomers in the bulk solution surrounding the micelles and the aggregated surfactant monomer in the micelle. The perturbation of this equilibrium leads to the so called fast relaxation time $\tau_f$ [80 - 82]. This relaxation occurs in the time range of $10^{-6} - 10^{-9}$ seconds. The relaxation spectra of micellar solutions are actually characterized by two distinct relaxation times $\tau_1$ and $\tau_2$.

The slow relaxation time lies in the time scale of second to millisecond region which is up to three orders of magnitude less than that of $\tau_1$. The relaxation time $\tau_2$ is identified as due to the step-wise build up of micelles from monomers and the dispersion of micelles into monomers [83].

In the present study on aqueous solutions of taurocholic acid and taurodeoxycholic acid, the absorption data obtained in the frequency range $3 - 89 \text{ MHz}$ fits very well to the equation for single relaxation which is shown in the figures 3.5 to 3.14. Thus, the solutions containing these bile salts in the concentration range studied obey Debye type of single relaxational behavior. This behavior is similar to the relaxation studies undertaken by Aicart et al [68] and Ravichandran et al [84] in aqueous and aqueous – ethanolic mixtures of DTAB and aqueous solutions of sodium.
taurocholate. This relaxation behavior is attributed to the exchange of surfactant monomer between the mixed micelle and the surrounding bulk solution.

A similar result of single relaxation behavior has been reported by Kato et al [62] for aqueous alkyltrimethyl ammoniumbromides in the frequency range 0.2 – 210 MHz. This study also established that the observed relaxation process is due to the exchange process of a surfactant monomer between alkyltrimethyl ammoniumbromide micelles and the surrounding bulk solution. Also in the present study on aqueous solutions of taurocholic acid and taurodeoxycholic acid the relaxation frequency $f_r$ shifts to a higher value with increasing concentration of the taurocholic acid and taurodeoxycholic acid and the relaxation time $\tau$ shifts to a lower value with increasing concentration of taurocholic acid and taurodeoxycholic acid. This behavior is in agreement with the studies of Kato et al [62]. Hence it may be inferred that the observed single relaxation behavior in the aqueous solutions of taurocholic acid and taurodeoxycholic acid may be due to the exchange of taurocholic and taurodeoxycholic monomer between the taurocholic and taurodeoxycholic micelle and the surrounding bulk solution.

Further it can be seen from the tables 3.3 and 3.4 that the computed values of relaxation time $\tau$ lie in the time scale of $10^{-8}$ seconds. The relaxation time which occurs in the time range of $10^{-4}$ to $10^{-9}$ seconds is associated with monomer micelle exchange [49, 50 & 85, 86]. This confirms that the single relaxation process observed in the aqueous solutions of taurocholic acid and taurodeoxycholic acid in the frequency range 3 – 89 MHz may be due to the monomer exchange between the taurocholic and taurodeoxycholic micelle and surrounding bulk solution.
3.2.5. ESTIMATION OF KINETIC PARAMETERS FOR THE FAST RELAXATION PROCESS:

The kinetic parameters for the fast relaxation process can be estimated by applying some of the relations derived from a general model of micelle formation and obtained from the expression for the relaxation time $\tau$ of the fast exchange process as [24, 80, 87]

$$\left(\frac{1}{\tau}\right) = 2\pi f_r = \left(\frac{k_{-1}}{\sigma^2}\right) + \left[\left(\frac{k_{-1}}{m}\right)\left(\frac{c}{c_1} - 1\right)\right]$$

where $c$ and $c_1$ are the total and monomer concentration of the surfactant respectively. Usually, $c_1$ is assumed to be equal to the critical micelle concentration. $m$, $\sigma^2$ and $k_{-1}$ represent the mean aggregation number, the variance of the size distribution on proper micelles and the mean dissociation rate constant respectively. For the maximum absorption per wavelength $(\alpha \lambda)_{\text{max}}$, the following expression has been derived by Teubner [87] on the basis of the kinetic model proposed by Aniansson and Wall [24b, 80]

$$(\alpha \lambda)_{\text{max}} = \frac{\pi \rho u^2 (\Delta \nu)^2 c_1 \left(\frac{\sigma^2}{m}\right) \left(\frac{c}{c_1} - 1\right)}{2RT \left[1 + \frac{\sigma^2}{m\left(\frac{c}{c_1} - 1\right)}\right]}$$

where $(\alpha \lambda)_{\text{max}}$ is defined as

$$(\alpha \lambda)_{\text{max}} = \frac{Af u}{2}$$

in the above equation, $(\Delta \nu)$ represents the isotropic volume change due to the exchange process, $\rho$ is the density of the solution, $R$ is the gas constant, $T$ is the temperature and $u$ is the ultrasonic velocity respectively.
Using the above equations, dissociative rate constant \( (k_i) \) and the volume change \( (\Delta v) \) are estimated. The value of the associative rate constant \( (k_i) \) is further estimated on the basis of the assumption

\[
k_i = \frac{k_{-i}}{c}
\]

The kinetic parameters for the monomer - micelle exchange process viz., standard volume change \( (\Delta v) \), associative rate constant \( (k_i) \) and dissociative constant \( (k_{-i}) \) are estimated using the above relations and are given in table 3.5 for taurocholic acid and taurodeoxycholic acid.

3.2.6. CONCLUSION:

The ultrasonic velocity studies in aqueous solutions of taurocholic acid and taurodeoxycholic acid indicate that the ultrasonic velocity increases with increasing concentration for taurocholic acid. The ultrasonic velocity increases with increasing solute concentration and a decrease in \( 0.004 \text{ mol dm}^{-3} \) and further increase in velocity from \( 0.005 \text{ mol dm}^{-3} \) for taurodeoxycholic acid. The plot of ultrasonic velocity against concentration shows a discontinuity at \( 0.007 \text{ mol dm}^{-3} \) for taurocholic acid and break at \( 0.004 \text{ mol dm}^{-3} \) for taurodeoxycholic acid, which corresponds to the critical micelle concentration of taurocholic acid and taurodeoxycholic acid in water. The increase in ultrasonic velocity may be due to the formation of taurocholic and taurodeoxycholic micelle in water. The possible interaction in the formation of taurocholic and taurodeoxycholic micelle may be due to the polyfunctional hydrogen bonding. The variation of adiabatic compressibility and intermolecular free length supports the explanation offered for velocity variation for taurocholic acid and taurodeoxycholic acid.

The ultrasonic absorption studies carried out in the frequency range 3 – 89 MHz shows that the ultrasonic absorption decreases with increasing frequency and shows a non-linear variation with increasing concentration. The absorption variation follows a
single relaxational behavior. The possible relaxation mechanism in the present study case may be due to the exchange of taurocholic and taurodeoxycholic monomer between taurocholic and taurodeoxycholic micelle and the surrounding bulk solution.
<table>
<thead>
<tr>
<th>x (mM)</th>
<th>ρ (Kgm⁻³)</th>
<th>ηₚ (x 10⁻³ Nsm⁻²)</th>
<th>u (ms⁻¹)</th>
<th>βₚ (x 10⁻¹⁰ N⁻¹m²)</th>
<th>$\frac{\alpha}{f^2}$ clₜ (x 10¹⁵ Npm⁻¹s²)</th>
<th>Lᵣ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>995.94</td>
<td>0.7975</td>
<td>1510.07</td>
<td>4.403</td>
<td>6.210</td>
<td>1.324</td>
</tr>
<tr>
<td>0.001</td>
<td>996.72</td>
<td>0.7877</td>
<td>1511.31</td>
<td>4.392</td>
<td>6.025</td>
<td>1.322</td>
</tr>
<tr>
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<td>997.10</td>
<td>0.7949</td>
<td>1512.03</td>
<td>4.386</td>
<td>6.069</td>
<td>1.321</td>
</tr>
<tr>
<td>0.003</td>
<td>997.68</td>
<td>0.7983</td>
<td>1512.30</td>
<td>4.381</td>
<td>6.088</td>
<td>1.320</td>
</tr>
<tr>
<td>0.004</td>
<td>998.16</td>
<td>0.8027</td>
<td>1513.27</td>
<td>4.374</td>
<td>6.107</td>
<td>1.319</td>
</tr>
<tr>
<td>0.005</td>
<td>998.65</td>
<td>0.8060</td>
<td>1513.99</td>
<td>4.368</td>
<td>6.121</td>
<td>1.318</td>
</tr>
<tr>
<td>0.006</td>
<td>998.94</td>
<td>0.8073</td>
<td>1515.00</td>
<td>4.361</td>
<td>6.116</td>
<td>1.317</td>
</tr>
<tr>
<td>0.007</td>
<td>999.13</td>
<td>0.8101</td>
<td>1515.43</td>
<td>4.358</td>
<td>6.131</td>
<td>1.317</td>
</tr>
<tr>
<td>0.008</td>
<td>999.61</td>
<td>0.8137</td>
<td>1517.07</td>
<td>4.346</td>
<td>6.135</td>
<td>1.315</td>
</tr>
<tr>
<td>0.009</td>
<td>1000.10</td>
<td>0.8168</td>
<td>1517.98</td>
<td>4.339</td>
<td>6.145</td>
<td>1.314</td>
</tr>
<tr>
<td>0.010</td>
<td>1000.48</td>
<td>0.8187</td>
<td>1519.04</td>
<td>4.331</td>
<td>6.144</td>
<td>1.313</td>
</tr>
</tbody>
</table>

x = concentration; ρ = density; ηₚ = shear viscosity; u = velocity; 
βₚ = adiabatic compressibility; $\left(\frac{\alpha}{f^2}\right)_{clₜ}$ = classical absorption; Lᵣ = free length;
Table 3.2
Ultrasonic velocity and related parameters for aqueous taurodeoxycholic acid

<table>
<thead>
<tr>
<th>x</th>
<th>ρ</th>
<th>η_s</th>
<th>u</th>
<th>β_s</th>
<th>( \frac{\alpha}{f^2} )_{cla}</th>
<th>L_f</th>
<th>A°</th>
</tr>
</thead>
<tbody>
<tr>
<td>mM</td>
<td>Kgm^{-3}</td>
<td>x 10^{-3} Nsm^{-2}</td>
<td>Ms^{-1}</td>
<td>x 10^{-10} N^{-1}m^2</td>
<td>x10^{-15} Npm^{-1}s^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.000</td>
<td>995.94</td>
<td>0.7975</td>
<td>1510.07</td>
<td>4.403</td>
<td>6.210</td>
<td>1.324</td>
<td></td>
</tr>
<tr>
<td>0.001</td>
<td>996.91</td>
<td>0.7934</td>
<td>1515.86</td>
<td>4.365</td>
<td>6.013</td>
<td>1.318</td>
<td></td>
</tr>
<tr>
<td>0.002</td>
<td>997.29</td>
<td>0.7996</td>
<td>1516.97</td>
<td>4.357</td>
<td>6.044</td>
<td>1.317</td>
<td></td>
</tr>
<tr>
<td>0.003</td>
<td>997.58</td>
<td>0.8014</td>
<td>1517.64</td>
<td>4.352</td>
<td>6.048</td>
<td>1.316</td>
<td></td>
</tr>
<tr>
<td>0.004</td>
<td>998.07</td>
<td>0.8034</td>
<td>1518.56</td>
<td>4.344</td>
<td>6.050</td>
<td>1.315</td>
<td></td>
</tr>
<tr>
<td>0.005</td>
<td>998.57</td>
<td>0.8051</td>
<td>1516.83</td>
<td>4.352</td>
<td>6.080</td>
<td>1.316</td>
<td></td>
</tr>
<tr>
<td>0.006</td>
<td>999.03</td>
<td>0.8066</td>
<td>1517.69</td>
<td>4.345</td>
<td>6.078</td>
<td>1.315</td>
<td></td>
</tr>
<tr>
<td>0.007</td>
<td>999.23</td>
<td>0.8094</td>
<td>1518.27</td>
<td>4.341</td>
<td>6.091</td>
<td>1.314</td>
<td></td>
</tr>
<tr>
<td>0.008</td>
<td>999.52</td>
<td>0.8105</td>
<td>1519.33</td>
<td>4.334</td>
<td>6.085</td>
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</tr>
<tr>
<td>0.009</td>
<td>999.90</td>
<td>0.8126</td>
<td>1520.01</td>
<td>4.328</td>
<td>6.090</td>
<td>1.313</td>
<td></td>
</tr>
<tr>
<td>0.010</td>
<td>1000.19</td>
<td>0.8150</td>
<td>1520.88</td>
<td>4.322</td>
<td>6.096</td>
<td>1.311</td>
<td></td>
</tr>
</tbody>
</table>

x = concentration; ρ = density; η_s = shear viscosity; u = velocity;

β_s = adiabatic compressibility; \( \frac{\alpha}{f^2} \)_{cla} = classical absorption; L_f = free length;
Table 3.3
Computed ultrasonic absorption related parameters for aqueous tauroholic acid

<table>
<thead>
<tr>
<th>x (mM)</th>
<th>f_r (MHz)</th>
<th>A x 10^{-15}</th>
<th>B x 10^{-15}</th>
<th>\tau (s)</th>
<th>(\alpha \lambda)_{max} x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>8.75</td>
<td>46.88</td>
<td>0.712</td>
<td>1.81</td>
<td>3.099</td>
</tr>
<tr>
<td>0.002</td>
<td>9.00</td>
<td>45.23</td>
<td>1.090</td>
<td>1.76</td>
<td>3.077</td>
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<tr>
<td>0.003</td>
<td>9.13</td>
<td>42.88</td>
<td>1.009</td>
<td>1.744</td>
<td>2.960</td>
</tr>
<tr>
<td>0.004</td>
<td>9.50</td>
<td>41.46</td>
<td>0.601</td>
<td>1.67</td>
<td>2.980</td>
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<tr>
<td>0.005</td>
<td>9.66</td>
<td>43.32</td>
<td>0.463</td>
<td>1.64</td>
<td>3.167</td>
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<tr>
<td>0.006</td>
<td>10.00</td>
<td>40.26</td>
<td>1.029</td>
<td>1.59</td>
<td>3.049</td>
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<tr>
<td>0.007</td>
<td>10.44</td>
<td>41.12</td>
<td>2.490</td>
<td>1.52</td>
<td>3.252</td>
</tr>
<tr>
<td>0.008</td>
<td>11.88</td>
<td>38.33</td>
<td>0.649</td>
<td>1.34</td>
<td>3.454</td>
</tr>
<tr>
<td>0.009</td>
<td>12.19</td>
<td>40.92</td>
<td>0.310</td>
<td>1.30</td>
<td>3.785</td>
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<tr>
<td>0.010</td>
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<td>37.69</td>
<td>0.451</td>
<td>1.21</td>
<td>3.758</td>
</tr>
</tbody>
</table>

x = concentration; f_r = relaxation frequency; A & B = relaxation amplitudes; \tau = relaxation time; (\alpha \lambda)_{max} = absorption per maximum wavelength;
Table 3.4
Computed ultrasonic absorption related parameters for aqueous taurodeoxycholic acid

<table>
<thead>
<tr>
<th>x (mM)</th>
<th>f_r (MHz)</th>
<th>A x 10^{-15}</th>
<th>B x 10^{-15}</th>
<th>\tau x 10^{-8}</th>
<th>(\alpha \lambda)_{max} x 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>8.45</td>
<td>50.90</td>
<td>1.890</td>
<td>1.88</td>
<td>3.375</td>
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<tr>
<td>0.002</td>
<td>8.94</td>
<td>50.66</td>
<td>0.116</td>
<td>1.78</td>
<td>3.435</td>
</tr>
<tr>
<td>0.003</td>
<td>9.31</td>
<td>45.11</td>
<td>0.193</td>
<td>1.71</td>
<td>3.186</td>
</tr>
<tr>
<td>0.004</td>
<td>9.81</td>
<td>43.72</td>
<td>1.042</td>
<td>1.62</td>
<td>3.256</td>
</tr>
<tr>
<td>0.005</td>
<td>10.25</td>
<td>42.71</td>
<td>1.823</td>
<td>1.55</td>
<td>3.320</td>
</tr>
<tr>
<td>0.006</td>
<td>11.25</td>
<td>40.86</td>
<td>3.012</td>
<td>1.41</td>
<td>3.488</td>
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<tr>
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<td>3.649</td>
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<tr>
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<td>1.34</td>
<td>3.674</td>
</tr>
<tr>
<td>0.009</td>
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<td>33.64</td>
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<td>3.275</td>
</tr>
<tr>
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<td>13.03</td>
<td>31.68</td>
<td>4.221</td>
<td>1.22</td>
<td>3.139</td>
</tr>
</tbody>
</table>

x = concentration; f_r = relaxation frequency; A & B = relaxation amplitudes; \tau = relaxation time; (\alpha \lambda)_{max} = absorption per maximum wavelength;
Table 3.5
Kinetic Parameters for aqueous taurocholic acid and aqueous taurodeoxycholic acid

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$\Delta v$</th>
<th>$k_1 \times 10^6$</th>
<th>$k_{-1} \times 10^9$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taurocholic Acid</td>
<td>17</td>
<td>2.6</td>
<td>3.8</td>
</tr>
<tr>
<td>Taurodeoxycholic Acid</td>
<td>12</td>
<td>2.2</td>
<td>3.1</td>
</tr>
</tbody>
</table>

$\Delta v =$ volume change; $k_1 =$ associative rate constant; $k_{-1} =$ dissociative rate constant
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